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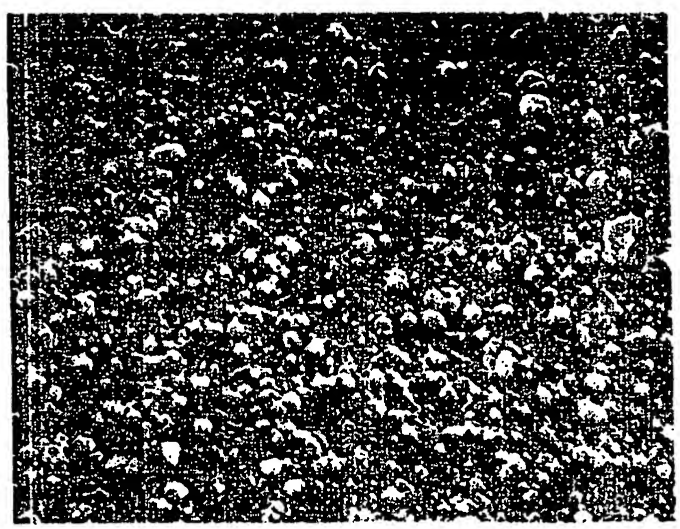

(57) Abstract

Flexible elastomeric articles such as surgeons' gloves include a slip-conferring coating to contact the user's skin or other tissue, the coating comprising a binder with microparticles adherently distributed therein, the particles having an oil absorption of at least 80g/100g, the coating having surfactant on its exposed surface. Microparticle materials include silica and other inorganic powders, and synthetic polymers such as polyamides and cellulose acetate.

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FLEXIBLE ELASTOMERIC ARTICLE WITH ENHANCED LUBRICITY

This invention relates to elastomeric flexible articles (e.g. film articles) that exhibit enhanced lubricity ("slip") with respect to both dry and damp surfaces, particularly skin or other tissue of the wearer, as compared to similar articles or films that are not treated as described herein.

Elastomeric surfaces of articles, in general, exhibit poor lubricity with respect to a dry surface, such as dry skin or other mammalian tissue. These properties are due to surface friction. Additionally, many elastomeric articles or surfaces display poor lubricity with respect to damp surfaces.

A high surface friction coefficient is useful for many applications such as tyre treads, flooring and footwear. However, these same properties are a distinct disadvantage in many other applications and especially in those applications wherein an elastomeric surface must slide on another surface, such as in the donning of gloves over dry or damp skin. This is particularly important in the use of medical gloves, such as examination gloves and surgeons gloves. These gloves are relatively close-fitting in order to provide sensitivity. Furthermore, most surgeons don their gloves after scrubbing up and without having fully dried their hands, so that areas of their hands may be dry

while other areas may be distinctly damp. Consequently, the elastomeric materials useful in such applications must exhibit simultaneously enhanced lubricity both to dry surfaces (dry slip) and to damp surfaces (damp slip), as well as the requisite mechanical properties (flexibility, strength, etc.).

Conventionally, dry slip is achieved by the use of powder lubricants such as magnesium carbonate, starch and talc. However, if the hands are damp, the use of a powder is counter-productive and may actually inhibit donning. Furthermore, in surgery, there is a risk of loose powder contaminating the surgical field. These materials can also cause irritation and may be allergenic.

Chlorination of rubber has also been proposed for the purpose of reducing tackiness and decreasing the coefficient of friction of rubber (see Romberg, "Aqueous Chlorination of Natural Rubber Surfaces", A.C.S. Rubber Division, Spring Meeting (1986); T.C.Q. Noakes, Proc. Int. Rubb. Technol. Conf., Penang, Malaysia (1988); Natural Rubber Technical Information Sheet No. 17, The Malaysian Rubber Producers' Research Association, Latex Series (1977); D.C. Blackley, "High Polymer Latices", Maclaren and Sons Ltd. (1966), p.548, and PCT/GB92/00171, published as WO 92/13497). However, chlorination can adversely affect the mechanical properties of flexible elastomeric articles such as rubber gloves and is better avoided for this reason. In addition, chlorination generally produces surfaces which have very poor damp slip.

Polymeric lubricant coatings which are bonded to the tissue-contacting glove surface or are embedded in the rubber itself have been proposed for the purpose of reducing surface friction of rubber in, for example, U.S. Patent Nos. 3,813,695; 3,856,561; 4,070,713; 4,143,109; and 4,302,852. U.S. Patent No. 3,813,695, in particular, describes a laminated surgical glove having a flexible outer layer and a hydrophilic plastic (hydrogel polymer) inner layer. Other

articles such as catheters and bathing caps coated with hydrophilic polymers are described in U.S. Patent Nos. 3,326,742; 3,585,103; 3,607,433; 3,745,042; 3,901,755; 3,925,138; 3,930,076; 3,940,533; 3,966,530; 4,024,317; 4,110,495; and 4,125,477 as well as British Patent Publication Nos. 1028446 and 859297.

James et al., U.S. Patent Nos. 4,499,154 and 4,575,476, describe treating a rubber article having a coating of a lubricated hydrogel polymer (inherently providing dry slip) bonded layer, with a surfactant material, such as a quaternary ammonium cationic surfactant, or a long chain fatty amine material to improve the lubricity of the coating with respect to damp skin.

U.S. Patents 4,143,109 and 4,070,713 and British Patent 1,541,155 (Arbrook patents) propose the use on the skin-contacting surface of an elastomeric medical glove of a second layer of elastomeric material bearing partially-embedded particulate matter (cross-linked starch particles or polyethylene, or ethylene-vinyl acetate copolymer particles 5-40 microns in size). The elastomeric material forming the second layer is said to adhere to both the particles and the elastomeric glove substrate. Carboxylated styrene-butadiene latex, brominated butyl rubber and styrene-polyethylene/butylene-styrene block copolymer are disclosed as specific elastomeric materials suitable for use in forming the particle-bearing layer. We have tested these gloves and whilst the dry lubricity is improved, there remains a tendency for the formation of a powdery deposit on the hand in use of the gloves. As described above, this is particularly undesirable in gloves for medical and surgical uses. Furthermore, the damp slip of these gloves is not very high.

Whilst the Arbrook patents correctly identify the need to secure the particulate matter in the elastomeric material of the glove the products described do not provide adequate adhesion. We have investigated this problem and

have now found that the securement of the particulate matter can be greatly improved. In particular, we have found that for adequate adhesion, the particulate matter must have a minimum porosity.

According to the present invention, there is provided a flexible article for use in contact with mammalian tissue, which article comprises a substrate layer of elastomeric material having a dry slip-conferring coating bonded thereto, the coating comprising a binder having microparticles adherently distributed therein, the microparticles having an oil absorption of greater than 80g oil per 100g microparticles, the coating having a surfactant on its exposed user-contacting surface.

The flexible elastomeric articles of the invention include those adapted for use in partial or total contact with mammalian tissue, such as surgical, examination and dental gloves, condoms, bandages, catheters, ureters, sheaths, and sheath-type incontinence devices and other film articles. Furthermore, the dry slip-conferring coating can be provided on more than one surface of the article if desired.

For purposes of this description, the outer surface of an article and, in particular, a glove, is defined as that surface which becomes an external surface of the glove in the position of actual use when worn. The inner surface is defined as that surface which is adjacent to the skin of the wearer when worn. The reverse is true in the case of a catheter or ureter: the outer surface is the surface in contact with the wearer's tissue. To avoid ambiguity, the term "wearer-contacting" surface will be used herein. "Tissue" includes skin or epithelia without limitation.

In the present invention, the substrate elastomer of the elastomeric flexible articles may be a natural or synthetic rubber. Without limitation, examples of synthetic rubbers are polyurethane, polyacrylate, polybutylene, and

silicone rubbers and block copolymers of monomers such as styrene and butadiene. Polyurethane and natural rubber are preferred, with polyurethane being most preferred. Typical thicknesses of the elastomer substrate for surgical gloves are within the range 30 to 200 microns, without limitation, with 100-150 microns being preferred.

The material used for the binder should have good adhesion to both the elastomeric substrate and to the microparticles and should preferably not adversely affect the mechanical properties of the article. Moreover, the binder layer should be resistant to the conditions of article manufacture and use. Clearly, the choice of the binder will depend, in substantial measure, on the nature of the substrate elastomer and of the microparticles. We have found, however, that by limiting the thickness of the coating relative to the thickness of the substrate and using correspondingly small, porous, absorbent microparticles, a variety of binder materials can be used. Although it is possible to obtain adequate dry-slip properties using a thicker coating and/or one that shows poor adhesion to the substrate, this is not desirable because such a coating shows a tendency to break up to some extent on deformation of the article (such as is incident to normal use, e.g. during donning in the case of a glove) and therefore suffers from the same disadvantages as use of powder lubricants.

When the substrate is a polyurethane and the microparticles are silica (which are preferred), the glass transition temperature of the binder polymer should be in the range of about -60 to about +30°C, preferably between about -5 and about +15°C. Preferred binder materials for a polyurethane substrate include polyurethanes, as well as copolymers and terpolymers of vinyl acetate (e.g. with ethylene, with ethylene acrylate, with ethylene and vinyl chloride, etc.).

When the substrate is natural rubber and the microparticles are silica, the glass transition temperature

of the binder polymer should be in the range of about -60 to about +30°C, preferably between about -15 and about +5°C. Preferred binder materials for a natural rubber substrate include copolymers and terpolymers of vinyl acetate (e.g., with ethylene, with ethylene acrylate, with ethylene and vinyl chloride, etc.).

The microparticles will generally have a size of from about 4 to about 20 microns, preferably with at least 30%, or more preferably at least 60% when polyurethane substrates are used, of the particles being within the range 5 to 13 microns. It is preferred that the particles have a relatively narrow size distribution. Particle size was measured on a weight percent basis (Coulter Counter, Industrial D Model) and/or on a volume percent basis (Malvern Master Sizer Model E, Malvern Ltd.)

They are preferably substantially regular in shape without sharp angles or edges (e.g. spherical or near spherical).

The preferred microparticles for use in the present invention are silica microparticles, especially (but not exclusively) those made by the gel technique. Examples of preferred silicas are Syloid ED5 and Syloid ED80 supplied by W.R. Grace & Co. Other materials can also be used provided they have the required porosity as measured by the oil absorption technique, and provided they are in other respects suitable for the intended use. We have found that other inorganic materials such as magnesium oxide can be used, as can certain synthetic polymeric materials such as polyamide powders and cellulose triacetate, for example. However, not all such materials which are commercially available have the necessary requirements for use in the present invention as will be clear to those skilled in the art. For example, none of the particular materials described in U.S. 4143109 for use as particulate matter (i.e. epichlorohydrin cross-linked corn starch, and polyethylene and ethylene-vinyl acetate beads) have the

necessary porosity. Routine testing will be required in any particular case to determine suitability. One problem which can arise with very fine particles is that they can be agglomerated, giving the appearance of a larger particle size than actually exists. Thus, particles that are really too small for use in the present invention can agglomerate to appear as "particles" of an appropriate size. Such agglomerates are not usually satisfactory in the present invention and their use should be generally avoided.

In the articles of the invention, the microparticles are firmly held by the binder so that their release in use of the articles is avoided. This firm holding is due to the relatively large porosity as measured by oil absorption. The particles create a roughened surface (as seen through an electron microscope) to the binder and it is believed that this surface effect is partly responsible for the improved slip obtained. One way of ensuring the formation of a roughened surface is to use a binder thickness of preferably not much greater than and most preferably slightly less than, the mean diameter of the microparticles. For example, if the microparticle diameter is 5 to 8 microns which, the most preferred binder thickness is about 4-5 microns which, for a 150- micron substrate, is 2-3% of the substrate, but the coating (including the particles enveloped by it) may be as thick as about 5% of the substrate, for example. In this way, the particles will protrude at the surface of the coating layer, to give a microroughened (globular reticulated) appearance to the coating (as seen under an electron scanning microscope). However, this size arrangement is not essential.

In the present invention, microparticle porosity can be measured in terms of oil absorption (DIN ISO 787/V). Microparticles having oil absorption values higher than about 80g/100g are suitable for use in the invention. Higher oil absorption values are preferred, e.g. 100g/100g., 180g/100g or even higher, e.g. above 280g/100g. The pore

volume should be preferably in the range 1 to 2 ml/g.

The concentration of microparticles used is preferably 10 to 40% by weight based on the binder composition. For medical gloves, the preferred range is 15 to 30%, with 20 to 25% being most preferred and 25% being best. Expressed alternatively, the binder:microparticle ratio is generally from about 1:1 (preferably about 2:1) to about 5:1. For medical gloves, a ratio of about 3:1 is most preferred. It will be appreciated by those skilled in the art that this amount is subject to optimization for a particular article according to the invention. In other words, the optimum concentration of microparticles will vary, depending on (i) the use to which the flexible elastomeric article is to be put, and (ii) the composition of the elastomeric article.

The surfactant used to endow the wearer-contacting surface with damp slip may be any surfactant which is suitable for use on skin or other tissue and does not cause an allergic, irritant, or other undesirable reaction in said skin or other tissue. Thus, in principle, amphoteric, anionic, cationic and nonionic surfactants, and long-chain fatty amines can be used, as taught for example in the various patents and patent applications referred to herein, to which reference should be made. However, in general, nonionic surfactants are found to be less effective than the other types and are not recommended as a class (although individual members of this class may be quite effective). Anionic surfactants, namely those comprising at least one lipophilic moiety such as an alkyl, aralkyl, aryl, or cycloalkyl group containing 8 to 18 carbon atoms, and a hydrophilic moiety such as a carboxylic, phosphoric, sulfonic, sulfuric, or other acid group or salt thereof, generally provide adequate damp slip properties but such surfactants are not preferred as a class because they show a marked tendency to cause irritation to skin and tissue at concentrations effective to provide damp slip.

Suitable cationic surfactants include those comprising at least one lipophilic moiety such as an alkyl, aralkyl, aryl, or cycloalkyl group containing 6 to 18 carbon atoms, and a hydrophilic moiety such as a substituted ammonium group (for example, a tetra-alkylammonium, pyridinium, or like group). The counter-ion present should be compatible with the tissue of the wearer; it could be, for example, chloride or other halide.

Preferred cationic surfactants are quaternary ammonium compounds having at least one C_8-C_{18} hydrocarbyl (alkyl, aryl, aralkyl or cycloalkyl) group; a preferred hydrocarbyl group is a hexadecyl group. The hydrocarbyl group may be attached to a quaternary nitrogen atom which is part of a heterocyclic ring (such as a pyridine, morpholine, or imidazoline ring).

Most preferred cationic surfactants are benzalkonium chlorides, hexadecyltrimethylammonium chloride, hexadecylpyridinium chloride, duodecylpyridinium chloride the corresponding bromides, and a hydroxyethylheptadecyl-imidazolium halide.

Suitable amphoteric surfactants include: betaines and sulteines containing at least one C_6-C_{18} hydrocarbyl group. Other types of suitable surfactants are amine oxides, sulfosuccinates and isethionates containing at least one C_6-C_{18} hydrocarbyl group. Amphoteric surfactants are preferred because they generally have a low skin irritancy potential.

Mixtures of surfactants may also be used.

A particularly preferred surfactant is hexadecyl pyridinium chloride, and other particularly preferred surfactants are coconut alkyldimethylammonium betaine and coco aminopropyl betaine.

In a preferred embodiment, the surfactant is bacteriocidal or bacteriostatic. The use of such a surfactant serves to inhibit bacterial growth when the layer formed on the coating is in contact with the skin or tissue

of the wearer. This is especially an advantage for surgeon's gloves because they are sometimes punctured during surgical procedures, and any bacteria which may have grown on a surgeon's skin since commencement of the operation may be released into the surgical field.

When a neutral fatty amine is used, a C_6-C_{18} hydrocarbyl group, such as a hexadecyl group, is preferably attached to the nitrogen atom. Such an amine is N-N-dimethylhexadecylamine.

The coating of surfactant or long chain fatty amine need not coat the wearer-contacting surface completely. It is only necessary that enough surfactant or long-chain amine is applied to enhance damp slip. It is preferred, to the extent that it is practicable, to keep the surfactant on the wearer-contacting surface, in the case of medical or dental gloves, in order to ensure that maximum grip is maintained on the outer surface. The surfactant can be applied as an aqueous solution containing from about 0.2 to about 2% surfactant. The article can be dipped in such solution or the solution can be sprayed or painted on it, preferably before it is removed from the former. Alternatively, the surfactant can be applied after the article is stripped from the former.

The process for applying the particle-containing coating to the wearer-contacting surface of the elastomeric substrate depends, in part, on the nature of the substrate and on whether the glove or other article is formed by dipping a former into an elastomeric polymer latex or into a solution of the elastomeric polymer in a suitable solvent. Methods for making the elastomeric substrate articles of the present invention are well-known in the art.

Where the article is formed from compounded natural rubber latex, the deposit on the former is beaded and leached in the normal way and may then be partially or fully dried but not fully vulcanized. It is envisaged that

the coating will normally be applied by subsequently dipping the deposit on the former into an aqueous suspension of the coating material, i.e. the binder and microparticles. The deposit and coating may then be heated to dry them and to complete vulcanization of the rubber.

In some cases, it may be advantageous to spray or paint a suspension or solution of the coating material on to the deposit on the former. Where spraying is used, it may be convenient to spray the rubber deposit first with a suspension or solution of the binder, dry the deposit, spray with a suspension of the microparticles, dry again, and spray once more with the binder and carrier, followed by final drying and vulcanization.

Other substrate polymers in dispersed, e.g. latex form, including polyurethanes, may be treated similarly, although a vulcanizing step will not be needed in every case, as can be readily appreciated by those skilled in the art.

When the article is formed by dipping from a polymer in solution, for example, a polyurethane in tetrahydrofuran, the deposit on the former is partially freed from solvent by heating and is then dipped into an aqueous suspension of the coating material and dried in the manner already described. In this case, also, the coating may be applied by spraying or painting, rather than dipping.

It is understood that various optional ingredients may be incorporated in these articles as apparent to those skilled in the art. For example, where the article is a glove an antiblock agent may be used which would facilitate donning and use. The antiblock agent is preferably a low-melting wax (mp. from about 100°C to about 150°C) such as polyethylene wax added as an aqueous emulsion (e.g. 1-2%) to the coating mixture. The particle size of the wax should be preferably less than 1μm to avoid interference with the surface morphology.

In order that the invention may be more fully understood, reference is made to the accompanying drawings, wherein:

Figure 1 is a photomicrograph taken through a scanning electron microscope (SEM) showing the microparticle-bearing binder layer of one preferred embodiment of the present invention. Noteworthy is that the coating has a substantially smooth yet microroughened appearance essentially free of sharp angles, cracks and craters;

Figure 2 is the same type of photomicrograph as Fig.1 wherein the binder layer contains microparticles of a different type and presents sharp angles;

Figure 3 is the same type of photomicrograph as Fig. 1 containing microparticles of yet a different type and presenting a "cratered" surface;

Figure 4 is the same type of photomicrograph as Fig. 1 showing a coating containing another type of microparticles and also presenting a cratered surface.

Figure 5 is the same type of photomicrograph as Fig. 1 showing a binder layer containing corn starch microparticles according to the prior art. Noteworthy is the presence of cracks and disruptions throughout the surface; and

Figure 6 is the same type of photomicrograph as Fig. 1 showing a coating finish similar to that of Fig. 1 on a natural rubber substrate.

In the following Examples, which illustrate the invention without limiting its scope, the following product designations are used:

FK383 precipitated silica (Trade Mark of Degussa Ltd.)
Sipernat 50S precipitated silica (Trade Mark of Degussa Ltd.)
Silosiv A10 zeolite (Trade Mark of W.R. Grace & Co.)
Syloid ED2 silica (Trade Mark of W.R. Grace & Co.)
Syloid ED5 silica (Trade Mark of W.R. Grace & Co.)

Syloid ED80 silica (Trade Mark of W.R. Grace & Co.)
Syloid 622 silica (Trade Mark of W.R. Grace & Co.)
Vinamul 3692 vinyl acetate/ethylene acrylate copolymer (Trade Mark of Vinamul Ltd. Carshalton, Surrey, England).
Vinamul 3231 vinyl acetate/ethylene copolymer (Trade Mark of Vinamul Ltd.)
Vinamul 3452 vinyl acetate/ethylene/vinyl chloride terpolymer (Trade Mark of Vinamul Ltd.)
Vinamul 3459 vinyl acetate/ethylene/vinyl chloride terpolymer (Trade Mark of Vinamul Ltd.)
Estane 5707 polyurethane (Trade Mark of B.F. Goodrich Inc.)
Witcobond 787 polyurethane aqueous emulsion (Trade Mark of Witco Chemical Corporation, New York, New York).
21P40 carboxylated styrene butadiene rubber (Trade Mark of Doverstrand Ltd., Harlow Essex, England).
Dehyton AB30 amphoteric surfactant (coconut alkyldimethylammonium betaine, Trade Mark of Henkel Ltd.).
Cross-linked corn starch was from Tunnel Refineries, Greenwich, London
Non-cross-linked corn starch was from Biosorb, Arbrook/Ethicon, U.K.
Aquaslip 655 or 671 polyethylene emulsion (Capricorn Chemicals, Ely, Cambridgeshire, U.K.).
HK 125/400 (Degussa)
Dehydol TA 20, non-ionic surfactant (Henkel)
Witcobond 769 Aqueous polyurethane (Witco)
Doverstrand 76D41 (Doverstrand)
Kraton D1117 styrene-isoprene-styrene block copolymer (Shell Chemicals, U.K.)
DC193 Silicone surfactants (Dow Corning)

The characteristics of finished films or articles were determined as follows:

Tensile strength, breaking elongation (EB), and

stress at 100% strain (S100) were measured according to ASTM D412. Tear strength was measured on angle test pieces (ASTM D624).

Adhesion of the binder to the substrate and adhesion of the particles to the binder were assessed visually using a scanning electron microscope (magnification 1.5×10^2 to 2.5×10^3). The samples were evaluated visually based, respectively, on the presence and frequency of cracks in the coating and on "crater" formation in the coating (the latter indicating that particles had been dislodged and therefore did not adhere to the binder). They were then rated on an arbitrary scale from 1 to 5 with 1 signifying "excellent" and 3 signifying "barely acceptable".

Dry slip and damp slip were evaluated subjectively on a scale of 1 (excellent slip) to 5 (no slip - undonnable in the case of a glove) with 3 being "barely acceptable".

EXAMPLE 1:

A film article (glove) was made by dipping a hand-shaped former into an 18% solution of a polyurethane in tetrahydrofuran (single dip process). While in the wet gel state (partially dried), and still on the former, the article was dipped into an aqueous coating solution containing 2.0% silica microparticles (Syloid ED5), 6.0% vinyl acetate/ethylene acrylate copolymer (Vinamul 3692; Tg+13°C), 0.1% xanthan gum, and 91.9% deionized water (all percentages being by weight). It was dried for 20 minutes at 100°C. While still on the former, the dried glove was dipped into a 0.75% aqueous solution of an amphoteric surfactant (Dehyton AB30) for 10 minutes. It was then stripped from the former and air-dried. The thickness of the coating in this Example was about 5 microns; the thickness of the binder alone was 4-5 microns.

The finished glove had tensile strength 60.3MPa and tear strength 60.1N/mm, compared with 62.9MPa and 59.6N/mm respectively, for a similarly prepared but uncoated

glove. Its dry slip rating was 1 and its damp slip rating 2.5. Excellent adhesion of the coating to the polyurethane (as well as of the particles to the binder) was demonstrated by scanning electron microscopy which showed a microroughened surface containing no cracks of the coating, no free fragments, and no craters (Figure 1).

EXAMPLES 2-6

Coated polyurethane gloves were prepared as in Example 1 except that the Vinamul 3692 was substituted by one of the binders shown in Table 1, which shows the dry slip rating and degree of adhesion achieved in each case.

TABLE 1

ADHESION OF VARIOUS BINDERS TO THE POLYURETHANE SUBSTRATE

Example No.	Binder	Tg (°C)	Adhesion
2	Vinamul 3231	0	1
3	Vinamul 3459	21	2
4	Vinamul 3452	30	3
5	Witcobond 787	-50	1
6	Estane 5707	about -40	1

EXAMPLES 7-13

Coated polyurethane gloves were prepared as in Example 1 except that the Syloid ED5 was substituted by one of the microparticles listed in Table 2 below. The dry slip ratings and degrees of adhesion achieved in each case are set forth in Table 2.

TABLE 2

EFFECT OF VARIOUS MICROPARTICLES ON PROPERTIES OF POLYURETHANE GLOVES

Ex. No.	Particle Type	Mean Diameter	Pore Volume ml/g	Oil Absorption g/100g	Dry Slip	SEM
1	Syloid ED5	5µm	1.8	320	1	Fig.1
7	Syloid ED80	8µm	1.8	300	1	
8	Syloid 622	12µm	1.2	180	1.5	
9	Syloid ED2	2µm	1.8	320	2.5	
10	FK383	1-2µm	N/A	220	3	Fig.2
11	Syloid AL1	8µm	0.4	80	3	Fig.3
12	Sipernat 50S	8µm	N/A	330	3.5	
13	Corn Starch (X-linked)	5-40µm	N/A	58	2-3	Fig.4

As can be seen from Table 2, the particles in Examples 1,7 and 8 performed most satisfactorily. Particles of Examples 9 and 10 were small and in addition may have been agglomerated (i.e. not of substantially smooth shape) and this may account for the highly angular appearance of the resulting coating (Fig. 2). In Example 11 the particles had very low oil absorption and yielded a coating with craters (Fig. 3). In Example 12, particle size range and distribution were very broad (for example, particles as large as 50µm and as small as 1µm were routinely seen on

SEM and the proportion of 8μm particles was relatively small), and this may account for the poor slip properties of the coating.

The corn starch particles in Example 13 also yielded a coating with craters indicating that the particles had become dislodged (Fig. 4). Their oil absorption was also low.

EXAMPLE 14 (Comparison Example):

Coated polyurethane gloves were prepared as in Example 1 except that the aqueous coating dispersion contained 1.5% crosslinked corn starch, 7.5% 21P40, 0.005% xanthan gum, 0.6% casein, 0.4% zinc oxide, and 90.0% deionized water, (according to U.S. Patent 4,143,109) and the dried glove was dipped into deionized water (no surfactant) for 10 minutes prior to stripping. The finished glove had satisfactory physical properties but its dry slip rating was 2-3. Adhesion of the coating to the substrate was poor, judged by its extensively cracked appearance (Fig. 5) and the fact that much of the coating had become detached during the water treatment prior to stripping. The finished glove had the appearance and feel of a powdered glove.

EXAMPLES 15-16:

A glove was made from high-ammonia natural rubber latex by a procedure known to those skilled in the art and involving the steps of dipping a hand-shaped former into an aqueous coagulant, air-drying, and dipping into the latex. The wet gel deposit was then dipped into one of the coating dispersions described in Examples 1 and 2. It was then dried and vulcanized by heating for 1/2 hour at 120°C. The properties of the finished gloves are described in Table 3.

TABLE 3

EFFECT OF VARIOUS COATINGS ON THE PROPERTIES OF NATURAL RUBBER GLOVES

Example No.	Coating of Example No.	Dry Slip	Adhesion
15	1	2	3
16	2	2	1

As can be seen from the above Table, softer binders (i.e. binders with lower Tg) are needed to accomplish the same adhesion when natural rubber substrate is used. Figure 6 illustrates the adhesion and appearance of a glove according to Example 16. It can be seen that the finish is equivalent to that of Example 1. However, much harder binders are also acceptable on polyurethane substrates.

EXAMPLE 17 (Comparison Example):

A glove was made from natural rubber latex by the method described in Examples 15-16 except that the coating was that of Example 14 (U.S. Patent 4,143,109). The adhesion of this coating in the finished glove was marginally better (rated 4.5) than that of Example 14 but the slip properties and appearance were the same.

EXAMPLE 18 (Aqueous Phase):

A glove was made from a polyurethane emulsion (Witcobond 787) by the general method described in Examples 15 and 16, dipping the wet gel into the coating dispersion described in Example 1. The adhesion of the coating was rated 1 and dry slip was rated 1.

EXAMPLES 1A, 7A 8A-13A and 19

The procedures of Examples 1 and 7-13 were repeated except as specified below:

Mean diameter was measured both as a weight percentage basis and on a volume percentage basis. In addition, the particle distribution was measured, using the Malvern apparatus. Finally, precipitated silica particles HK 125/400 were added to the materials tested. This material was tested by the procedure of Example 1 except that the coating contained 1.5% HK 125/400; 2.0% Aquaslip 671 polyethylene emulsion containing 40% solids; 4.5% V3692 (50% solids); 0.2% xanthan gum; about 1% Dehydol TA 20 (20% solids) in 8 litres of deionized water. This material gave good adhesion (2) to the polyurethane substrate. The results are set forth in Table 2A.

In a separate experiment, Syloid 622 produced good

adhesion and a dry slip of "1" on a natural rubber substrate. The foregoing results yield the following conclusions:

Oil absorption should be fairly high (at least over 80/100). A narrow particle size distribution is preferred, the narrower the better. As important as the oil absorption and more important than the distribution is the use of nonagglomerated particles: FK 383 and HK 125/400 are both agglomerated particles made up of smaller (10-30nm) primary particles.

Stability of the dispersion in the binder is also a factor, as illustrated below.

TABLE 2A:

EFFECT OF VARIOUS MICROPARTICLES ON PROPERTIES OF POLYURETHANE GLOVES

Example Number	Particle Designation	Manufacturer	Mean Particle Diameter (microns) and Distribution (Volume %)				Oil Absorption	Pore Volume (ml/g)	Dry Slip on Polyurethane
			Measured by Coulter (wt.%)	Measured by Malvern (vol.%)	in 4-20 micron range	in 5-13 micron range			
1A	Syloid ED5	Grace	5	8.8	87	61	308	1.8	1
7A	Syloid ED80	Grace	8	11.1	75	45	300	1.8	1
8A	Syloid 622	Grace	12	12.8	59	33	180	1.2	1.5
9A	Syloid ED2	Grace	2	4.2	54	26	320	1.8	2.5
10A	FK 383	Degussa	1-2	7.6	57	37	230	N/A	3
11A	Syloid AL1	Grace	8	N/A	N/A	N/A	80	0.4	3
12A	Sipernat 50S	Degussa	8	19.8	47	26	326	N/A	3.5
13A	Corn Starch (non-cross-linked)	Biosorb	5-40	14.4	75	28	58	N/A	2-3
19	HK 125/400	Degussa	N/A	9.6	85	55	220	N/A	2

EXAMPLE 20: EFFECT OF DIFFERENT SUBSTRATES

Three alternative substrates to natural rubber and polyurethane were tested with a particularly preferred coating for adhesion and dry slip: Witocbond 769 Aqueous Polyurethane; Doverstrand 76D41 self cross-linking styrene-butadiene latex; and Shell Kraton D1117 styrene-isoprene-styrene block co-polymer in tetrahydrofuran.

These materials were cast onto glass plates using a K bar and partially dried (15-30 mins at 70°C). The films, whilst still firmly adhered to the glass plate, were then dipped into the following coating formulation:

0.5% Solid wax (A671)
1.5% Silica (ED5)
4.0% Solid binder (V3692)
0.25% Xanthan Gum
1.0% Solid Dehydol TA 20
0.9% DC 193 silicone surfactants

The coated films were then dried for 30 mins. at 100°C. The films were stripped from the plate with the aid of water and coating quality/adhesion was assessed visually. The results are in Table 4.

TABLE 4

EFFECT OF DIFFERING SUBSTRATES ON COATING ADHESION/SLIP

	Adhesion	Dry Slip
Witcobond 769	Good	1
Doverstrand 76D41	Good	1
Kraton D1117	Good	1

As can be seen all performed well and would be suitable as alternative substrates. Adhesion testing was visual and a "good" rating roughly corresponds to 2 in Table 1. Coating quality and dry slip properties were similar to those obtained on polyurethane.

EXAMPLES 21 TO 28

In the following Examples, the following additional product designations are used:

Beetle 9040 (Aliphatic Aqueous PU (ex BIP)
Laurapal X1207 Non-ionic wetting agent (ex Witco)
Biosorb non-crosslinked corn starch
Microthene FN510 polyethylene micro beads (ex Croxton and Garry)
Microthene FE532 Ethylene/Vinyl Acetate micro beads (ex Croxton and Garry)
Magnesium oxide (fine) (ex Aldrich)
Aluminium oxide (light) (ex Aldrich)
Celluflow TA25 Micronised porous cellulose triacetate (ex Presperse Inc.)
Orgasol 2002 UD Micronised porous polyamide (ex ELF Atochem) (5 microns)
Orgasol 2002 EXD Micronised porous polyamide (ex ELF Atochem) (10 microns)
Kraton G1650 Styrene - Ethlylene - Butylene - Styrene (ex Shell Chemicals)
Brominated Butyl rubber latex (ex Burke Palmerson VH14/163)
Antioxidant 2246 [2,2'-methylene-bis(4-methyl-6-t-butylphenol)]

Oil absorption measurements were carried out on various types of particles according to ISO 787/V. The results are given in Table 5 and show that the particles used in the Arbrook patent had oil absorption values well below the minimum 80g/100g of those used in the present invention. Apart from aluminium oxide, the remaining particles had oil absorption values of 100g/100g or above.

TABLE 5

OIL ABSORPTION OF VARIOUS PARTICLES

Particle	Oil Absorption g/100g
Non-crosslinked Corn Starch (Arbrook)	40
Polyethylene powder (Microthene FN510) (Arbrook)	50
EVA powder (Microthene FE532 (Arbrook)	51
Magnesium oxide	140
Aluminium oxide	34
Polyamide powder (Orgasol 2002 UD)	120
Polyamide powder (Orgasol 2002 EXD)	100
Cellulose triacetate (Celluflow TA25)	115

The particle size distributions of these particles were measured using a Malvern photon correlation spectrometer (Master Sizer Model E). The results, expressed on a volume basis, are given in Table 6. All the particles had a mean size within the preferred range of 4-12 microns.

TABLE 6

PARTICLE SIZE DISTRIBUTION DATA

Particle	Mean Particle Size µm	Proportion between 3 and 20µm(%)	Proportion between 5 - 13µm (%)	Span *
Magnesium oxide	4.9	76	55	1.68
Aluminium oxide	4.6	69	50	2.04
Polyamide powder (Orgasol 2002 UD)	4.8	74	50	1.68
Polyamide powder (Orgasol 2002 EXD)	10.2	78	58	1.86
Cellulose triacetate (TA25)	12.2	78	58	1.53

* Span is an arbitrary measure shown on the Malvern printouts which gives an indication of the breadth of particle size distribution. For wide distributions the number is large and conversely for small distributions the number is small.

EXAMPLES 21 AND 22 (Comparison)

Examples 2 and 3 from Arbrook U.S. Patent No. 4,143,109 were formulated as shown below.

Example 2 (Arbrook)

300g	Kraton G 1650
30g	Pale crepe natural rubber
300g	White mineral oil
6600g	Toluene
300g	Crosslinked corn starch
7530g	Total (represents approx. 1:1 particle: binder ratio)

The Kraton G was dispersed in 2200g of toluene using a paddle stirrer. This process was repeated with the crepe rubber and the starch. The three mixtures were then blended together in an 8-litre dipping pot. The dispersion was covered and left to stand overnight but was stirred vigorously immediately before dipping.

Example 3 (Arbrook)

300.00g	Brominated butyl rubber (solid)
10.50g	Stearic acid
3.75g	Antioxidant 2246
15.00g	Paraffin wax
75.00g	Finely divided talc
6.00g	Petroleum Jelly
6.00g	Titanium dioxide
15.00g	Zinc oxide
3.00g	Zinc dimethyldithiocarbamate
375.00g	Microthene FN510 polyethylene
7500.00g	Hexane
8309.25g	Total (represents approx. 1:1 particle: binder ratio)

Brominated butyl rubber latex was dried down to form solid brominated butyl rubber which was comminuted and dissolved in 2000g of hexane. To this solution were added petroleum jelly and paraffin wax. A clear solution without lumps or gels was formed. The remaining ingredients (except

the Microthene) were dispersed in 200g of hexane and then blended into the solution. Microthene beads were dispersed in the remaining hexane and blended with the stirred bulk dispersion. After a further period of stirring, the dispersion was placed in a dipping pot and covered. The dispersion was left to stand but was stirred immediately prior to dipping.

The stabilities of the dispersions produced in Arbrook Examples 2 and 3 were tested immediately and 24 hours after mixing. The results are given in Table 7. The dispersions were applied to glove formers which had previously been coated with a thermoplastic polyester polyurethane by dipping into a tetrahydrofuran solution (18%) and drying for 30 min. at ambient temperature. After dipping into the dispersion, the film was dried and treated as described in Example 1. The adhesion of the coating to the polyurethane substrate and the slip properties of each glove are described in Table 7.

Neither of the Arbrook Examples provided an acceptable slip coating. The particles were not well bonded to the substrate, probably because they did not absorb the binder adequately (low oil absorption). The surfaces they provided were granular and showed poor slip. This is ascribed to the relatively large size of the particles (described by the manufacturer as having a mean diameter of about 20 microns).

EXAMPLE 23

Magnesium oxide (13g) was dispersed in deionised water (400g) using a paddle stirrer, and xanthan gum (2g) was dispersed in deionised water (400g) using a Silverson mixer. These two mixtures were blended together by gentle stirring. Vinamul 3692 (78g) (binder) was added to the resulting dispersion and stirred thoroughly. The mixture was made up to 1 litre using deionised water and placed in a dipping pot. Dispersion stability was checked as before (Table 6). A polyurethane film was coated by dipping into

this dispersion as in Examples 21 and 22 except that a condom former was used. Adhesion and slip properties are given in Table 7.

TABLE 7

STABILITY OF DISPERSIONS AND COATING CHARACTERISTICS

Example Number	Formulation	Dispersion Stability		Adhesion to Substrate	Slip Properties	"Feel"
		0 h	24 h			
21	Arbrook Ex2	O.K.	Settled	Inconsistent coverage; very patchy. Flakes off particularly when wet.	Poor and "draggy" (4)	Very granular and distinctly rough
22	Arbrook Ex3	O.K.	Settled	Better coverage than Ex 2. More consistent. Can be easily abraded.	Poor (3-4)	Very granular and rough
23	Magnesium oxide	Flocculated	Flocculated	Generally good but poorer in agglomerated areas	Acceptable (2.5)	Very granular, grainy
24	Magnesium oxide (high pH)	Flocculated	Flocculated			
25	Aluminium oxide	O.K.	Settling	Poor wetting. Sheen finish as per straight V3692, suggesting poor pick up of Al_2O_3	Inconsistent; some drag. Barely acceptable (3)	Feels powdery
26	Cellulose triacetate	O.K.	O.K.	Good/excellent	Excellent (1)	Slightly papery
27	Polyamide powder (Orgasol 2002 UD)	O.K.	O.K.	Excellent	Excellent (1)	Similar to ED5 system but slightly smoother
28	Polyamide powder (Orgasol 2002 EXD) (on natural rubber)	O.K.	O.K.	Excellent	Excellent (1)	As 2002 UD

EXAMPLES 24-27

This process was repeated with the following particles and modifications:

Magnesium oxide: The acidic Vinamul V3692 binder was replaced by an alkaline binder (Beetle 9040) and dilute ammonia added to raise the pH to that of aqueous magnesium oxide.

Aluminium oxide in place of the magnesium oxide (comparison Example).

Cellulose triacetate in place of magnesium oxide. Laurapal X1207 (2g) was also added to aid with dispersion of the powder in the Silverson mixer.

Polyamide (Orgasol 2002 UD) in place of magnesium oxide. Laurapal X1207 (2g) was also added to aid dispersion of the powder in the Silverson mixer.

EXAMPLE 28

The polyamide, Orgasol 2002 EXD was used in this Example in place of magnesium oxide and the condom former was dipped in natural rubber latex as in Examples 15 and 16. In this case the softer binder, Vinamul 3231, was used instead of Vinamul 3692.

The results in Table 7 show that aluminium oxide has too low oil absorption to form a good coating. Magnesium oxide was reasonably effective but its dispersions were rather unstable. The cellulose triacetate and both polyamides showed excellent adhesion and slip properties on both polyurethane and natural rubber substrates.

CLAIMS:

1. A flexible article for use in contact with mammalian tissue, which article comprises a substrate layer of elastomeric material having a dry slip-conferring coating bonded thereto, the coating comprising a binder having microparticles adherently distributed therein, the microparticles having an oil absorption greater than 80g oil per 100g microparticles, the coating having a surfactant on its exposed user-contacting surface.

2. An article according to claim 1 wherein the microparticles have an oil absorption of at least 180g oil per 100g microparticles.

3. An article according to claim 1 or 2, wherein the elastomer is natural rubber, a polyurethane, a polyacrylate, a polybutylene, a silicone rubber, or a block copolymer of styrene and butadiene.

4. An article according to claim 1, 2 or 3, wherein the binder is a polymer having a glass transition temperature higher than -60 and lower than +30°C.

5. An article according to claim 4, wherein the binder is a copolymer or terpolymer of vinyl acetate with at least one of ethylene, ethylene acrylate and vinyl chloride.

6. An article according to any of claims 1 to 5, wherein the microparticles have a mean diameter of 5 to 13 microns.

7. An article according to any of claims 1 to 6, wherein the surfactant is an alkyldimethylammonium betaine or a quaternary ammonium compound having at least one C_6-C_{18} hydrocarbyl group.

8. An article according to any preceding claim, wherein the microparticles are of an inorganic or synthetic polymeric material.

9. An article according to claim 8 wherein the microparticles are of silica, magnesium oxide, cellulose triacetate or polyamide.

10. An article according to any of claims 1 to 9, which is a medical or surgical glove.

Fig.1.

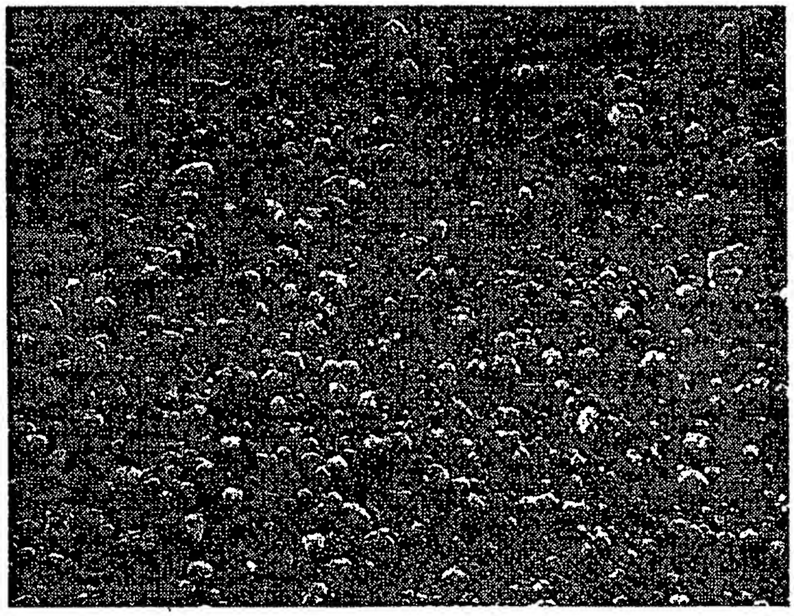

Fig.2.

Fig.3.

Fig.4.

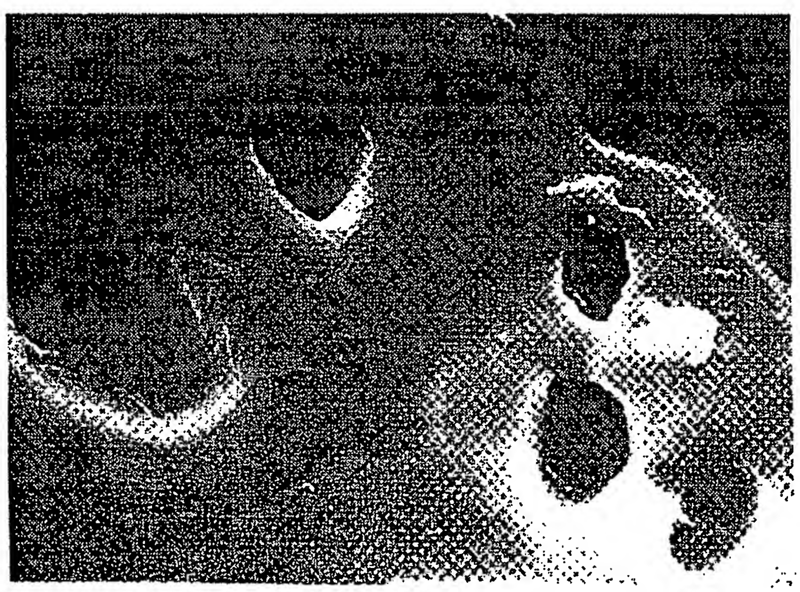

Fig.5.

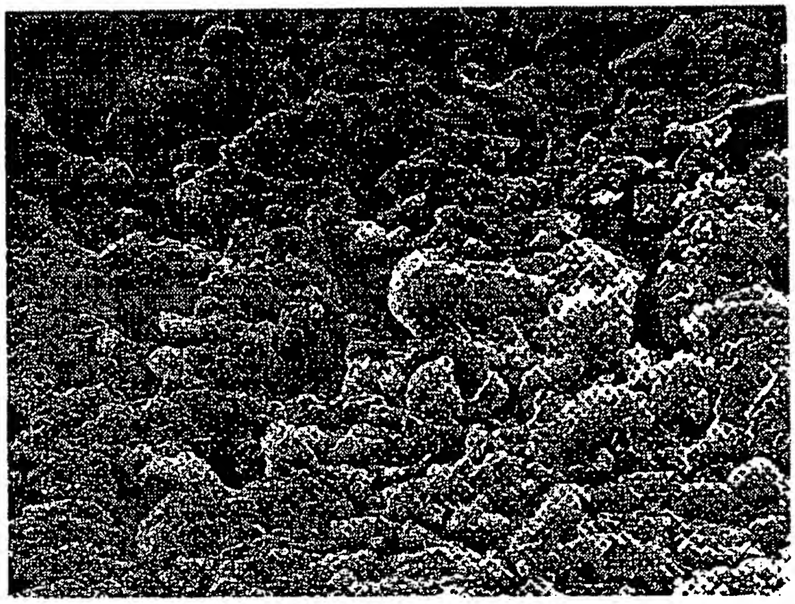

Fig.6.

INTERNATIONAL SEARCH REPORT

Inte nal Application No
GB 94/00031

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 A61L31/00 C08J7/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08J A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,88 08311 (SMITH & NEPHEW ASSOCIATED COMPANIES PLC) 3 November 1988 see claims 1-4,16,18 see page 14, line 1 - page 14, line 7 see examples 5,6 ---	1,3,8,10
A	US,A,4 070 713 (G.F. STOCKUM) 31 January 1978 cited in the application see claim 1 see figure 4 ---	1
A	EP,A,0 105 613 (LRC PRODUCTS LIMITED) 18 April 1984 see claims 1-4 & US,A,4 499 154 (LRC PRODUCTS LIMITED) cited in the application -----	1,7

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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1

Date of the actual completion of the international search	Date of mailing of the international search report
11 April 1994	28. 04. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hallemeesch, A

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 94/00031

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